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TECHNICAL REPORT

THE INFRARED ABSORPTION SPECTRUM OF WATER VAPOR AND CARBON DIOXIDE

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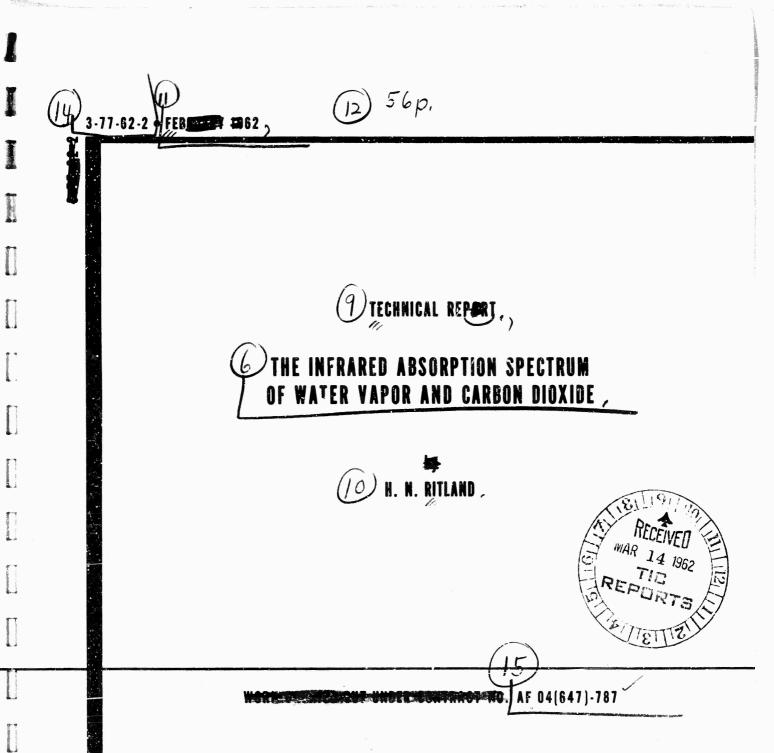
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⑨ TECHNICAL REPORT

⑥ THE INFRARED ABSORPTION SPECTRUM
OF WATER VAPOR AND CARBON DIOXIDE

⑩ H. N. RITLAND

WORK CARRIED OUT UNDER CONTRACT NO. AF 04(647)-787

Lockheed

MISSILES and SPACE DIVISION

LOCKHEED AIRCRAFT CORPORATION · SUNNYVALE, CALIF.

FOREWORD

This work was performed under Contract AF 04(647)-787
as an adjunct to a study of the atmospheric transmission
of infrared radiation.

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ABSTRACT

A brief review is given of the basic principles which govern the absorption of infrared radiation by molecules, with emphasis on the factors which govern the qualitative features of the observed spectra. This is used as a basis for the examination of the infrared spectra of water vapor and of carbon dioxide. The characteristics of the individual bands are discussed in terms of the underlying theory and are illustrated by experimental absorption curves derived from the published literature.

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Section 1

INTRODUCTION

This report deals with the general features of the infrared spectra of water vapor and carbon dioxide and is intended to aid in the understanding of their missile detection applications. Before discussing the individual spectra in detail, some basic facts connected with the absorption and emission of electromagnetic radiation by atoms and molecules should be considered.

It is well known that the total energy of an atom or molecule, apart from its purely translational kinetic energy, is restricted to a number of discrete values or "energy levels." These values can, at least in principle, be calculated for any system by the use of quantum mechanics. Each of these energy levels can be identified with a particular state of the atom or molecule; the lowest level or "ground state" is the most stable configuration. Higher levels correspond to varying degrees of electronic excitation or, if more than one atom is involved, of internal kinetic energy of the various parts of the molecule. In principle, a possible emission or absorption frequency is associated with every pair of levels (e.g., "A" and "B") through the quantum relation $E_A - E_B = h\nu$, where E is the energy of a given level and ν is the frequency of the electromagnetic radiation. In practice, it is found that only a small fraction of these possible radiation frequencies are actually observed; the specific combinations of levels which can radiate are governed by "selection rules" which can, again, be determined by quantum mechanics.

The energy levels of primary interest in optical and infrared spectra are those associated with excitation of the outer, or valence, electrons (qualitatively, their transfer to larger orbits) and with vibration and rotation of molecules. Experimentally, it is found that electronic excitation energies are usually of the order of several electron volts or more, while the rotation and vibration energies are considerably smaller. As the infrared spectrum, beyond approximately one micron, corresponds to a quantum

energy of the order of one electron volt or less (1 ev corresponds to 1.239 microns), we see that infrared radiation is associated primarily with the rotation and vibration of molecules. The shorter wavelengths (visible and ultraviolet), with their larger quantum energies, are primarily associated with electronic transitions, possibly accompanied in the case of molecules by vibration and rotation changes as well. This division is not strictly true — some higher order vibration transitions extend into the visible region (e.g., the atmospheric water bands and the Venus carbon dioxide bands). Also, many electronic transitions between highly excited states occur in the infrared. These exceptions are usually of secondary importance as they are relatively weak because of the low transition probability for the high-order vibration transitions or because of the small number of atoms or molecules in the excited states involved (particularly in absorption, in which in most cases only transitions from the ground state are observable).

This report, therefore, deals with infrared vibration and rotation spectra only. The basic features of these are determined by the mechanical makeup of the molecule — the number and arrangement of the atoms, and the forces between them. Using quantum mechanics, it is found that the overall symmetry of the molecule is of basic importance. The rotational energy levels are determined by the moment of inertia of the molecule about its principal axes; the vibrational levels are determined by the atomic motions and force constants involved in the normal vibrations of the molecule. (The vibration energies are basically simply $h\nu$, where ν is the frequency of the corresponding normal vibration.) The permitted transitions between the possible levels (vibration energy plus rotation energy), and hence the overall appearance of the spectrum, are determined by the requirement that the molecule either have a permanent dipole moment (in the case of rotation only) or that a changing dipole moment be produced in the course of the vibration, so that the molecule may interact with the electromagnetic field. The resulting "selection rules" are closely related to the symmetry characteristics of the molecule and of the vibrations involved.

This report is concerned only with water vapor and carbon dioxide. There are two reasons for this — the most important is their prominence both in rocket plume emission and in atmospheric absorption. In addition, they are very useful for illustrating the basic features of infrared spectra — carbon dioxide is a linear, highly symmetric molecule composed of fairly heavy atoms, while water is a nonlinear and hence rather unsymmetric molecule with the light hydrogen atoms. Therefore, they illustrate most of the points of importance in infrared spectroscopy.

The carbon dioxide spectrum is treated first, together with a discussion of symmetry requirements and selection rules. The water vapor treatment is somewhat less detailed, and presupposes a familiarity with the section on carbon dioxide and with the general principles enunciated therein. The emphasis in all cases is on the qualitative features which govern the overall features of the radiation or absorption. The general characteristics of the individual bands are illustrated with published curves from various sources, but no attempt is made to give a quantitative discussion of the absolute intensities of the bands.

Section 2

CARBON DIOXIDE

2.1 NORMAL VIBRATIONS

Carbon dioxide is a linear symmetric molecule, with the carbon atom in the center and the oxygen atoms at either end. The molecule has three normal modes of vibration:

v_1 ⬡— ● —⬡ $\nu = 1388 \text{ cm}^{-1}$ $\lambda = 7.21\,\mu$

v_2 ⬡——●——⬡ $\nu = 667.3 \text{ cm}^{-1}$ $\lambda = 15.0\,\mu$

v_3 ⬡— ● —⬡ $\nu = 2349.3 \text{ cm}^{-1}$ $\lambda = 4.26\,\mu$

The numbering of these and other sets of normal vibrations is set by the custom that the totally symmetric vibration with the highest frequency is v_1, with other vibrations following in order of frequency, followed in turn by the non-symmetric ones, with the exception that the bending vibration of a linear molecule is always designated as v_2.

Comments on the normal vibrations are listed below:

(a) The frequencies of the vibrations are qualitatively in the order of the force constants. The bending vibration has the least resistance to deformation and hence the lowest frequency. The vibration v_3 involves the most intimate contact and hence the highest frequency.

(b) The fundamental v_1 is not observed in the infrared. It is symmetric, and the molecule remains so in the vibration. Since no dipole moment is produced, it is impossible for the molecule to interact with the electromagnetic field and absorb or radiate energy. However, this fundamental is observed in the Raman effect and is also observed indirectly in the infrared in combination bands involving transitions in more than one of the normal vibrations at the same time.

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(c) The vibration v_2 is degenerate. There are two modes with exactly the same frequency – one in the plane of the paper and one perpendicular to it. In such a case, the vibration can be equally well described in terms of suitable linear combinations of the original normal modes. In particular, they can be combined to give rotating modes (by adding two planar vibrations with 90-deg phase difference). These modes have angular momentum about the axis of the molecule, which introduces symmetry properties which have considerable effect on the selection rules as will be seen below.

(d) Substitution of the heavier carbon 13 for carbon 12 has no effect on v_1 as the carbon atom remains stationary during the vibration; v_2 and v_3 are each reduced by about 3 percent by this substitution. The magnitude of the isotope effect is 68 cm^{-1} for v_3 and 19 cm^{-1} for v_2. The natural abundance of carbon 13 is about one percent of that of carbon 12, so the isotope bands are usually relatively weak.

(e) The frequency $2v_2$ is close to v_1. This leads to complications involving "Fermi resonance" in which two levels with approximately the same frequency and similar symmetry properties "mix" to form new combinations. This interaction produces a small shift in frequency of the resultant levels from the "original" locations and often makes a major change in the relative intensities of the various transitions involving these levels. This effect is analogous to the classical result that two coupled oscillators with the same natural frequency will exhibit two resonant frequencies, one above and one below the unperturbed frequency. (Examples are coupled pendulums and double-tuned i-f transformers.)

(f) The frequencies given are for the fundamentals, in which only one vibration is excited with one quantum of vibrational energy and with no rotational excitation. If the molecular forces were simple harmonic, the frequency would be independent of the degree of excitation; actually, the forces are somewhat anharmonic and decrease somewhat as the intermolecular separation increases. In effect, the presence of vibration "loosens" the molecule,

so the frequency of a given vibration is lowered. As a result, harmonics are not exactly integral multiples of the corresponding fundamentals, and a given vibrational transition is shifted to lower frequency (longer wavelength) when other vibrational modes are active even though they do not participate in the transition involved.

(g) The same is true regarding rotation. The carbon dioxide molecule can rotate about an axis perpendicular to its axis. The centrifugal force produced by the rotation stretches the molecule and reduces the vibration frequency accordingly. The shift is not large, but makes a pronounced change in the shape of the vibration-rotation bands as will be seen below.

2.2 ENERGY LEVELS AND SELECTION RULES

2.2.1 Rotation

Energy levels. The energy levels of a rigid rotator can be derived approximately from the fundamental requirement that the angular momentum of the molecule must be an integral multiple of $h/2\pi$:

$$I w = J h / 2\pi$$

$$E = \frac{1}{2} I w^2 = \frac{J^2 R^2}{8\pi^2 I} = B J^2 \tag{1}$$

where

$$B = \frac{h^2}{8\pi^2 I}$$

w = angular velocity

I = moment of inertia

J = an integer

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An exact quantum-mechanical calculation gives:

$$E(J) = BJ(J + 1)$$

B is called the "rotational constant"; it varies inversely with the moment of inertia of the molecule. The carbon dioxide molecule has only one (degenerate) rotational mode, about an axis perpendicular to the molecular axis, and hence has one rotational constant B which is approximately 0.4 cm^{-1}. (The value of B varies somewhat with vibrational excitation, and is smaller for higher vibrational states because of the larger moment of inertia associated with the stretched molecule.)

Selection rules. Normally, pure rotation transitions are allowed in which the quantum number J changes by plus or minus one. This produces a series of equally spaced lines:

$$\Delta E = E(J + 1) - E(J) = B(J^2 + 3J + 2) - B(J^2 + J) = 2BJ + 2B \qquad (2)$$

A different line results for each value of J; the line separation is 2B. However, the carbon dioxide molecule has no permanent dipole moment because of its symmetrical construction, and there is no mechanism for interaction between the rotating molecule and the electromagnetic field. Hence there is no pure rotation infrared spectrum for CO_2.

2.2.2 Vibration

Energy levels. If the amplitude of vibration is not too large, a molecule vibrates very nearly as a simple harmonic oscillator. (That is, the potential energy function is symmetrical about the equilibrium position; its form is quadratic, and the restoring force is proportional to the departure of the molecule from its equilibrium position.)

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The derivation of the allowed energy levels for such a vibrator is more difficult than the calculation of the rotational levels, as it requires solution of the Schrodinger equation for this potential function. When this is done, the allowed energy levels are found to be

$$E_n = \left(n + \frac{1}{2}\right)h\nu_{osc} \tag{3}$$

where $\nu_{osc} = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$ with k = the force constant, m the effective mass, and ν_{osc} is the frequency of the classical oscillation frequency for this harmonic oscillator.

The vibration state of a molecule is described by stating the number of quanta of vibrational energy in each normal mode. Thus the state $(2, 1, 3)$ is the one with two quanta in mode v_1, one in v_2, and three in v_3; $(0, 0, 0)$ is the ground state.

Selection rules. The selection rule for the simple harmonic oscillator is found to be

$$\Delta n = \pm 1, 0$$

The +1 corresponds to absorption, the -1 to emission. $\Delta n = 0$ obviously means no transition. As the energy levels are equally spaced, all transitions have exactly the same frequency in the harmonic oscillator approximation. This corresponds to the classical situation, where the frequency of a harmonic oscillator is independent of its amplitude (first observed by Galileo) and is in fact exactly the same frequency as the quantum-mechanical result.

If the molecule were a purely harmonic oscillator, the only infrared frequencies observed would be those fundamentals which are infrared active (v_2 and v_3 in this case). The small anharmonicity can be treated by introduction of another term in the equation for the inter-atomic potential function and solving the Schrodinger equation by a perturbation method.

The anharmonicity has a number of effects:

(1) The selection rule is relaxed somewhat and transitions with

$$\Delta n = \pm 2, \pm 3, \text{ etc.}$$

are allowed, although with progressively lower intensity than the fundamental. (These transitions are harmonics or overtones, analogous to the classical result.)

(2) Transitions between higher vibrational states have somewhat lower frequency than the 0 to 1 transition because of the flattening out of the potential function (i.e., loosening of the molecule.) Also, harmonics are no longer exactly integral multiples of the fundamentals.

(3) Combination bands are allowed (provided the symmetry of the vibrations permit). The intensities of these transitions, in which the excitation levels of two or more vibrations change simultaneously, are normally considerably lower than those of the fundamentals.

Temperature effects. The distribution of molecules among a number of possible energy states is given by the expression

$$n_i = \frac{N g_i e^{-E_i/kT}}{\sum_i g_i e^{-E_i/kT}}$$

where

n_i = number of molecules in state i

E_i = excitation energy of state i

g_i = degeneracy factor (number of substates with the same energy)

N = total number of molecules

Near room temperature, most of the molecules are in the ground state, so the sum in the denominator is approximately independent of temperature. The population of the excited states is then given predominantly by the Boltzmann factor $e^{-E_1/kT}$. At room temperature (300°K), the value of kT is equivalent to 209 cm^{-1}. The Boltzmann factors for the various normal vibrations of CO_2 are therefore:

$$v_1 \quad e^{-1388/209} \quad = \quad e^{-6.63} \quad = \quad 0.0013$$

$$v_2 \quad e^{-667/209} \quad = \quad e^{-3.19} \quad = \quad 0.04$$

$$2v_2 \quad e^{-1334/209} \quad = \quad e^{-6.38} \quad = \quad 0.0017$$

$$v_3 \quad e^{-2349/209} \quad = \quad e^{-11.2} \quad = \quad 1.2 \times 10^{-5}$$

It is seen that near room temperature, vibrations v_1 and v_3 are negligibly excited, while a few percent of the molecules have one quantum of v_2. We expect, therefore, to see some transitions such as $(0, 1, 0) \rightarrow (0, 1, 1)$ in absorption; these will be relatively weak and will have a strong temperature dependence because of the Boltzmann factor which governs the population of the v_2 level. Absorption bands originating from vibrationally excited states are often called "hot bands."

At higher temperatures, such as prevail in radiating sources, the situation is considerably more complicated; many of the vibration states are appreciably populated, and the sum in the denominator must be explicitly determined.

Symmetry considerations. The carbon dioxide molecule is a highly symmetric one, and the wave functions which determine the transition probabilities and the selection rules are correspondingly symmetric. A given vibrational state is characterized by the following:

    (a)   Angular momentum about the internuclear axis. The total angular momentum is an integral multiple, ℓ, of $h/2\pi$. States with $\ell = 0, 1, 2, 3$, etc., are designated Σ, Π, Δ, ϕ, etc., in correspondence with the atomic designations s, p, d, f. States with even ℓ are symmetric with respect to

reflection in a plane perpendicular to the axis of rotation (that is, they are unchanged); states with odd ℓ are antisymmetric (i.e., change sign on reflection). In the case of the carbon dioxide molecule, only vibrations in which v_2 is excited can have angular momentum; states with only v_1 or v_3 or combinations of them are necessarily Σ states.

(b) <u>Behavior of the wave function on reflection in a place containing the internuclear axis.</u> As the molecule is symmetric with respect to this operation, the only effect on the vibration wave function can be to leave it unchanged or to multiply it by (-1). (Only quantities involving the square of the wave function are observable.) States which are unchanged are $(+)$; states which change sign are negative $(-)$. This is a symmetry property only for the Σ states; states with angular momentum are degenerate and reflection can result in different linear combinations of the "original" states.

(c) <u>Behavior of the wave function on inversion in the origin.</u> The carbon dioxide molecule has a center of symmetry and the state can be either symmetric (unchanged) or antisymmetric (change sign) with respect to an inversion (i.e., exchange of x for $-x$, y for $-y$, z for $-z$). These states are designated g and u respectively, from the German "gerade" and "ungerade."

The following are examples of state designations for vibrations of the carbon dioxide molecule:

- Ground state $(0,0,0)$ is Σ_g^+; it is symmetric in everything and has no angular momentum.
- $(1,0,0)$, the state with one quantum of v_1 and no other vibrations excited, is also Σ_g^+; this is a symmetric vibration.
- $(0,0,1)$, with only v_3 excited, is Σ_u^+. All the action is still along the axis of the molecule so there is no angular momentum, and reflections perpendicular to the axis can have no effect (hence the state is still positive), but inversion "flips the vibration around."

● $(0, 1, 0)$, with one quantum of v_2, is Π_u. This is a degenerate vibration, with two modes at right angles to each other. Linear combinations of these vibrations can be made with one unit of angular momentum in either direction of rotation about the internuclear axis; hence they are Π states. The state is u because inversion interchanges the roles of the oxygen atoms; the + or − character is not defined, as reflection in a plane containing the molecular axis makes new linear combinations. One way of looking at it is that such a reflection changes the phase of the rotation by an amount depending on the instant at which the reflection occurs, rather than only by 0 or 180 deg.

The state designation gets more complicated when several quanta of excitation are involved, particularly for v_2. The state $(0, 2, 0)$, for example, has three degenerate sub-levels. As in the single excitation $(0, 1, 0)$, each quantum of v ational excitation in this mode is accompanied by one unit of angular momentum which we can designate by ↑ or ↓ for the two possible directions of rotation. These angular momenta can be combined to give ↑↓, ↓↑, ↑↑, and ↓↓. The first two are indistinguishable and hence, in reality, represent only one state. This state has no net angular momentum and is a Σ state; the other two have a net angular momentum of $2h/2\pi$ and are Δ states. Although in a harmonic oscillator all three states have the same energy, in a molecule the anharmonicity produces a separation between the Σ and Δ states. The two groups are often distinguished by writing $(0, 2^0, 0)$ and $(0, 2^2, 0)$, respectively, with the first Σ_g^+ and the second, doubly degenerate, Δ_g. Note for the v_2 vibration, even harmonics are g states and odd harmonics are u states.

It is perhaps in order to make a comment about the relation of symmetry properties to selection rules. The basic factor that determines the transition probability for a given (electron dipole) transition is the matrix element M defined by

$$M^2 = \int \psi_f^* \; e \; \vec{r} \; \psi_i \; d\tau \tag{4}$$

Here ψ_i is the wave function of the initial state in the transition, ψ_f that of the final state, and e $\vec{r}$ is the dipole moment. ($\vec{r}$ is the radius vector from the origin to the point of integration xyz.) The vector $\vec{r}$ is antisymmetric; it changes sign on inversion in the origin, and at least one component of it changes sign under other symmetry operations such as reflection in a plane. Therefore, if the initial and final wave functions are either both symmetric or both antisymmetric in regard to a given symmetry operation, the corresponding part of the vector r will give equal positive and negative contributions in the integration which determines the matrix element, and the integral will be zero — that is, the transition will not occur.

Another way of stating the requirement that the initial and final wave functions must be of different symmetry is the following: It is permissible for wave functions to change sign on reflection or on another symmetry operation, as the wave function itself is never observed; only the square of the absolute value of the wave function has physical meaning (that is, $\psi^*\psi$), and it is unchanged if the wave function itself is multiplied by -1. However, the quantity $M^2 = \int \psi^* \vec{r} \psi \, d\tau$ is also a physical quantity and an observable. Therefore, if the initial and final states have the same symmetry with respect to a given operation, the quantity M^2 will change sign under this operation because of the antisymmetric property of $\vec{r}$. A real physical quantity is obviously unchanged by a mere redefinition of coordinate system; hence M^2 must be zero, as zero is the only number which is unchanged when it is multiplied by -1.

The significance of these considerations in regard to vibrational transitions is that only those transitions take place which satisfy the following conditions:

$$\Delta l = 1, 0$$

$$g \leftrightarrow u \qquad g \not\leftrightarrow g \qquad u \not\leftrightarrow u \qquad (5)$$

$$\Sigma^+ \not\leftrightarrow \Sigma^-$$

where $\rightarrow\!\!\!\!\!\!\cdot$ means no transition. An example of the operation of these selection rules
is in the transition $(1, 0, 0) \rightarrow (0, 0, 0)$, which would radiate or absorb the frequency
v_1. The upper state is Σ_g^+ and the lower state is also Σ_g^+; this transition would
violate the rule $g \nrightarrow g$. Hence this transition does not occur in the infrared. We
have already said that it would not occur because the vibration v_1 does not produce
any dipole moment; the symmetry argument is a more elegant way of stating the same
thing in this simple case.

One additional symmetry requirement affects indirectly the infrared spectrum of the
carbon dioxide molecule. When the entire wave function is considered, it is symme-
tric or antisymmetric with respect to interchange of two identical particles, depend-
ing on whether the particles obey Bose statistics (e.g., 0^{16} nuclei with spin zero) or
Fermi statistics (e.g., electrons or hydrogen nuclei with spin $\frac{1}{2}$).

2.2.3 Vibration-Rotation Bands

Energy levels. In the first approximation, the total energy of the molecule, including
both vibration and rotation, is simply the sum of the rotational and vibrational energies:

$$E = E_{vib} + E_{rot} = \sum_i (n + 1/2) h \nu_i + B J(J + 1) \tag{6}$$

The exact expression for the energy levels is considerably more complicated, as the
interaction between vibration and rotation introduces terms allowing for the dependence
of rotational moment of inertia on the vibrational excitation and for the change of force
constant of the vibration on the amount of rotational excitation. These are usually
introduced in the form of quadratic terms in the various quantum numbers; they will
not be discussed here.

Selection rules. As a consequence of the much larger energies involved in vibrational
transitions as compared with rotational transitions, infrared spectra appear as "bands "

made up of a large number of lines corresponding to the same vibration transition but with different rotational initial and final states. In these compound transitions, to a first approximation, the selection rules for the vibration and rotation components are independently obeyed consistent with the overall symmetry requirements.

The basic vibration selection rules have been stated above in Eq. (5). The basic rotational selection rule is

$$\Delta J = \pm 1, 0 \qquad + \leftrightarrow - \tag{7}$$

Rotational levels with even J have positive symmetry; those with odd J are negative. The combination of vibrational and rotational selection rules results in three types of bands for the carbon dioxide molecule. These are described below.

(a) If both the initial and final state are Σ vibrational states, the rotational state must change in order to provide a change from $+$ to $-$ symmetry. For these bands, then, $\Delta J = \pm 1$; $\Delta J = 0$ is not allowed. $\Delta J = +1$ in emission means that the energy of the rotational transition subtracts from the vibration transition energy, and the resulting lines for various values of J are at longer wavelength than the band center; $\Delta J = -1$ in emission adds to the energy and gives a series of lines extending shorter wavelengths. These are called the "P branch" and "R branch," respectively; they can be remembered by noting that the R branch is not toward the longer wavelength or red side. This type of band is called a "parallel" band as the change in dipole moment is parallel to the axis of the molecule.

(b) If the initial and final states have different vibrational angular momentum, that is, $\Delta \ell = \pm 1$, the transition $\Delta J = 0$ is allowed in addition to $\Delta J = \pm 1$. To a first approximation, all the lines for different values of J have the same frequency if $\Delta J = 0$; this produces a "Q branch," which appears as an intense group of closely spaced lines at the center of the band. As the oscillating dipole is perpendicular to the molecular axis for the v_2 vibration, these are called "perpendicular bands."

(c) If $\Delta \ell = 0$ but $\ell \neq 0$ (for example, $\Pi - \Pi$ or $\Delta - \Delta$ bands), a third type of band results which has a weak Q branch of different character from the type (b) bands above. These are unimportant for this discussion, since they represent transitions between excited states and hence are very weak at room temperature. They will become important at higher temperatures, but under these conditions so many bands are involved that individual bands can usually not be distinguished.

Temperature effects and the shapes of bands. In contrast to the vibrational case, kT at room temperature is much larger than the rotation energy for small values of J. In a given sample of gas, therefore, molecules exist in considerable number of rotational states. The most probable value of J can be calculated by differentiating the following expression:

$$N(J) = g_J e^{-EJ/kT}$$

$$= (2J + 1) e^{-BJ(J + 1) hc/kT} \tag{8}$$

Here, g_J is the "degeneracy factor"; it is equal to $(2J + 1)$ for a rotation state with angular momentum $Jh/2\pi$. (This arises because the component of angular momentum along a given direction in space is also required to be an integral multiple of $h/2\pi$; it can therefore be J, $J - 1$, $J - 2 \ldots - J$, for a total of $2J + 1$ values.) Carrying out the differentiation, we obtain, setting

$$\frac{dN}{dJ} = 0 \qquad \left(2J_{max} + 1 \right)^2 = \frac{2}{B} \frac{kT}{hc} \quad \text{and} \quad J_{max} \approx \sqrt{\frac{1}{2B} \frac{kT}{hc}} \tag{9}$$

The locations of the lines for different initial and final values of J can be calculated by remembering from Section 2.2.1 that the rotational energy is given by $BJ(J + 1)$.

The transition energy is therefore, using J'' (or J) for the lower state and J' for the upper state:

$$E = E' - E'' = E_{v'} + B'J'(J' + 1) - E_{v''} - B''J''(J'' + 1) \qquad (10)$$

where E_v is the vibrational energy. If we set $B' = B'' = B$, we obtain:

- For $J' = J'' + 1$ (lower state lower rotational energy, R branch)

$$\Delta E_R = \Delta E_v + 2B + 2BJ$$

where $J = J''$ is the lower state quantum number.
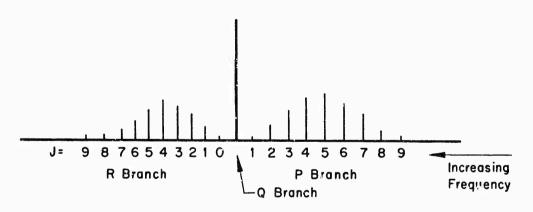
- For $J' = J'' - 1$ (P branch)

$$\Delta E_P = \Delta E_v - 2BJ \qquad (11)$$

- For $J' = J''$ (Q branch)

$$\Delta E_Q = \Delta E_v$$

independent of J.

Combining these, we obtain an overall band of the following form:

In this diagram, the height of the lines is an indication of their intensity. The intensity is proportional to the population of the rotational levels involved. Considering only the P and R branches, their intensity is small near the center of the band because of the small number of levels; they are fully populated but the degeneracy factor $2J + 1$ is

small. Far from the band center, the intensity is again small because of the large rotation energy compared with kT . The maximum intensity comes at the value of J calculated above in Eq. (9). The separation of the maximum from the band center is approximately $2BJ_{max}$ or

$$\Delta\nu = 2B\sqrt{\frac{1}{2B}\frac{kT}{hc}} = \sqrt{(0.8)(209)} = 13 \text{ cm}^{-1} \tag{12}$$

for carbon dioxide at room temperature. ($B = 0.4 \text{ cm}^{-1}$, $T = 300°K$, $kT/hc = 209 \text{ cm}^{-1}$.)

In the actual case, the rotational constant B' in the upper state is usually smaller than that for the lower state, B''. This arises because the molecule is more extended when it is vibrating (an effect coming from the anharmonicity of the potential) and hence has a larger moment of inertia and a smaller B . The expressions for the positions of the lines for the three branches then become:

P branch ($J'' = J' + 1$)

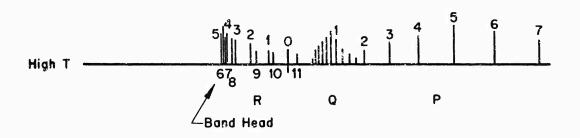$$\Delta E = \Delta E_v - (B'' - B') J - (B'' - B') J^2$$

R branch ($J'' = J' - 1$)

$$\Delta E = \Delta E_v + 2B + (3B' - B'') J - (B'' - B') J^2 \tag{13}$$

Q branch ($J'' = J'$)

$$\Delta E = \Delta E_v - (B'' - B') J(J + 1)$$

The effect is to add a term in J^2 to all three branches. The effect on the Q branch is to separate the lines into a closely spaced band. It adds to the separation of the lines in the P branch and stretches it out; it subtracts from the separation of the lines in the R branch and compresses it progressively as the distance from the band center increases. At a sufficiently high value of J , the separation becomes zero and then changes sign; at that value of J , the band "turns around" and forms a band

head. The appearance of the band at low temperature, with only a few J values excited, and at higher temperatures where many lines are active, is as follows:

Low T

    J = 5 4 3 2   1   0   1   2   3   4   5   6   7

    R   Q   P

High T

    5 4 3 2 1 0   1   2   3   4   5   6   7

    6 7 8   9 10 11

    R   Q   P

Band Head

2.3 CONSIDERATION OF INDIVIDUAL BANDS

2.3.1 4.3-Micron v_3 Fundamental Region

High resolution. Figure 2-1 shows a spectrum obtained by Dr. Norman Jones, National Research Council, Ottawa, and reported by Plyler (Ref. 1). The resolution is sufficiently high that each rotational line is individually resolved.

The following points are pertinent:

(a) The P and R branches are present, but no Q branch. This is consistent with the character of the states involved; the upper state, (0, 0, 1) is Σ_u^+; the lower, (0, 0, 0), is Σ_g^+.

(b) The lines with odd J (in the lower state) are missing. This can be verified from: (1) the line numbering on the figure and from the spacing which is 4B (1.6 cm^{-1}) instead of 2B, and (2) from a detailed examination of the
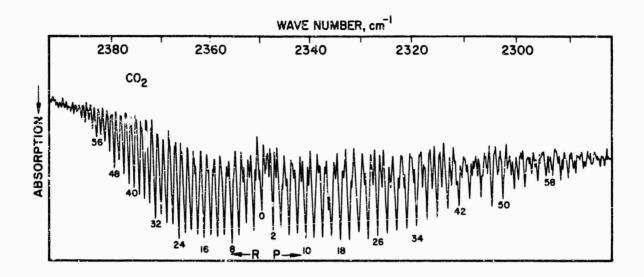
WAVE NUMBER, cm^{-1}

Fig. 2-1 Carbon Dioxide 4.3-Micron Band (v_3 Fundamental) at High Resolution. Data by Jones (Ref. 1)

relative line locations in the P and R branches. This is a consequence of the presence of the two identical oxygen atoms, with nuclear spin equal to zero. These obey Bose statistics, so the overall wave function must be symmetric with respect to interchange of the two oxygen nuclei. The electronic wave function is unchanged by such an interchange; the vibration wave function for the ground state, Σ_g^+, is unchanged while for the upper state Σ_u^+, the sign is changed; the rotation levels are unchanged for the positive levels (with even J) and changes sign for the negative levels (with odd J). The result of all these considerations is that a symmetric vibration state such as (0, 0, 0) can have only rotation levels with even J, while an antisymmetric vibration state such as (0, 0, 1) can have only odd J. Therefore, the alternate lines are missing, not because of a selection rule prohibiting the transition, but rather because there simply are no molecules in the corresponding rotation states. That this is a result of the nuclear identity is shown by the fact that a molecule with non-identical oxygen atoms, such as $CO^{16}O^{17}$, exhibits all the rotation lines, while a molecule with identical nuclei but with non-zero nuclear spin, such as $CO^{17}O^{17}$, exhibits all the lines but with an intensity alternation between even and odd J.

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(c) The line intensity is maximum for J between 10 and 20, consistent with the value calculated from Eq. (9):

$$J_{max} = \left[\frac{1}{2B} \frac{hc}{kT} \right]^{1/2} = 16$$

(d) The influence of the J^2 term in the line spacing is evident in the progressive spreading of the lines in the P branch with increasing J and the corresponding crowding of the R lines. Calculation shows that the line separation in the R branch becomes zero for $J = 127$ at $\nu = 2399$ cm^{-1}; this produces a band head at that wavelength at temperatures high enough to populate rotational levels of this magnitude.

(e) The short wavelength part of the spectrum (the R branch) is rather clean, but at longer wavelength the spectrum is more irregular in appearance because of the presence of additional lines in addition to the rotation transitions in the $(0, 0, 0) \rightarrow (0, 0, 1)$ band. These additional lines come primarily from the following bands:

$(0, 1, 0) \rightarrow (0, 1, 1)$ centered at 2337 cm^{-1} (7.4 percent population)

$(0, 2^2, 0) \rightarrow (0, 2^2, 1)$ centered at 2324 cm^{-1} (0.3 percent population)

They are lower in intensity because of the Boltzmann factor in the population density of the lower vibrational level at room temperature. As the temperature is raised, these additional bands increase in intensity, and others with more vibrational excitation appear. All of these bands are transitions with $\Delta v_3 = 1$, $\Delta v_1 = 0$, and $\Delta v_2 = 0$; the transitions with v_1 and v_2 are centered at progressively longer wavelength (lower frequency) because of the effect of the stretching of the molecule on the force constants.

Other room temperature measurements. Burch, Gryvnak, and Williams (Ref. 2) (henceforth referred to as Burch) have reported a number of curves showing the absorption of the 4.3-micron CO_2 band at medium resolution. Three of these are reproduced in Fig. 2-2.
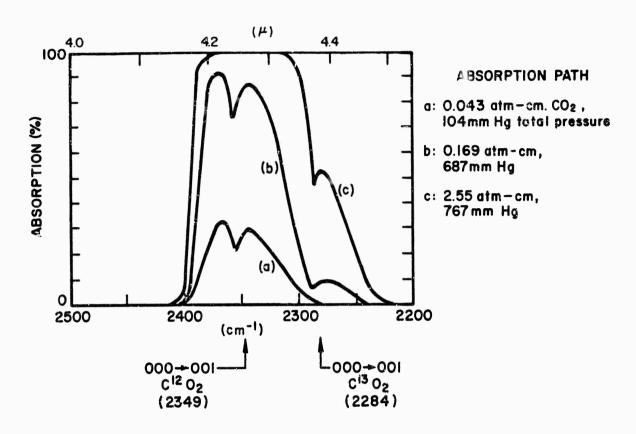
Fig. 2-2 Carbon Dioxide 4.3-Micron Band Under Medium Resolution. Data by
Burch et al. (Ref. 2)

Comments:

(a) At medium absorption, the band shows the P and R branches, with a
minimum in between. The absorption in the R branch is more intense
because of the closer spacing of the lines; it is narrower than the P
branch. At long path length where the absorption in the central region of
the band is essentially complete, the further growth of the band is primar-
ily to the long wavelength side because of the heading up of the R branch.
Taylor and Yates (Ref. 3) observed essentially complete absorption from
4. 18 to 4. 36 microns (2265 to 2390 cm^{-1}) over a 1000-foot path in the
atmosphere at sea level, and from 4. 18 to 4. 55 microns (2200 to 2390 cm^{-1})
over a 10-mile path.

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(b) At sufficiently long path lengths, the absorption by the $C^{13}O_2$ molecule is appreciable. (The concentration of carbon 13 is about one percent of that of carbon 12.) It is centered at longer wavelengths as discussed earlier.

Howard, Burch, and Williams (Ref. 4) reported measurements of the 4.3-micron region at lower resolution but with longer path lengths. Two of their curves covering a relatively wide wavelength region are shown in Fig. 2-3, with the locations of the centers of the various bands indicated.
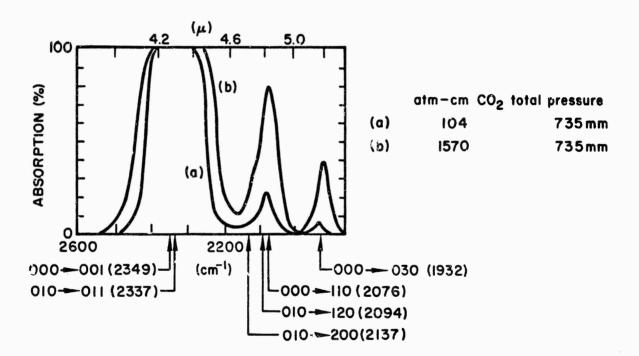
Fig. 2-3 Carbon Dioxide 4.3- 4.8- and 5.2-Micron Bands, Low Resolution. Data by Howard et al. (Ref. 4)

This shows the presence of three groups of bands in the 4.3-micron region:

$\Delta v_1 = 0$,	$\Delta v_2 = 0$,	$\Delta v_3 = 1$	The v_3 fundamentals, very intense
1	1	0	Combination band, weak
0	3	0	v_2 third harmonic, weak

All of these groups include bands originating in the ground state and "hot bands" originating from vibrationally excited states; the latter are much weaker at room temperature but increase in intensity rapidly with temperature. As was indicated in Section 2.2.2, only the vibration states $(0, 1, 0)$, $(0, 2, 0)$ and $(1, 0, 0)$ are appreciably populated at room temperature, in addition to the ground state $(0, 0, 0)$.

High temperature measurements and calculations. Spectral emissivity measurements on gases at high temperature are extremely difficult to make and there are relatively few curves available. Tourin (Ref. 5) has made an extensive study of the absorption of radiation by carbon dioxide in the 4.3-micron region using a heated absorption cell, but his report is not available to the writer at the present time. Ferriso (Ref. 6) has measured the emission from the plume of a small rocket constructed to give uniform conditions in the flame near the nozzle. He uses a double-path arrangement, measuring both emission and absorption, and hence can calculate the emissivity. One of his curves is given in Fig. 2-4.

It is seen that the band at this temperature extends to much longer wavelengths than at room temperature because of the effects of both high vibrational and high rotational excitation. (The dip in the curve near 4.3 microns is due to atmospheric absorption in the spectrometer.) As the measured emissivity is less than 1 even in the central band region, this is a real band broadening and not merely an apparent one as in the long path atmospheric transmission data.

Edwards (Ref. 7) has reported lower resolution data obtained with a heated absorption cell. His primary interest was in the determination of the total band strength for use in heat transfer calculations. One of his curves for the 4.3-micron region is shown in Fig. 2-5.

Again, the 4.3-micron band extends to longer wavelengths. The strength of the 4.8-micron band increases markedly because of the presence of hot bands in this region; the 5.2-micron harmonic band is less affected.
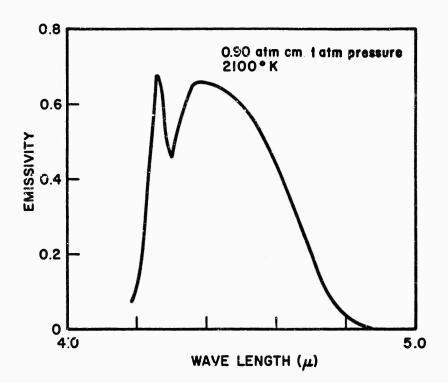
Fig. 2-4 Carbon Dioxide 4.3-Micron Band in Emission at 2100° K. Data
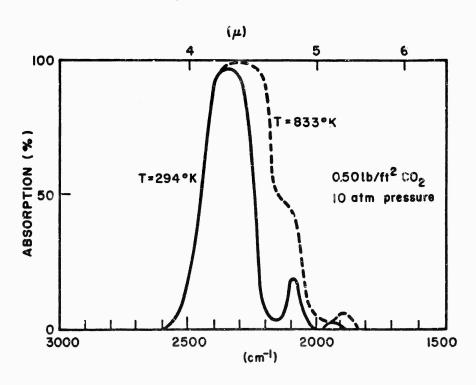by Ferriso (Ref. 6)

Fig. 2-5 Temperature Dependence of Carbon Dioxide 4- to 5-Micron Bands, Low
Resolution. Data by Edwards (Ref. 7)

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Plass (Ref. 8) has made extensive calculations of the emissivity of carbon dioxide at elevated temperatures. An indication of the complexity of the problem is given by the number of transitions involved; at 2400°K, he computed for 3549 vibrational transitions, with a total of 890,000 individual vibration-rotation lines. In general, the qualitative agreement of his calculated curves with experimental data is good; the quantitative agreement is excellent at temperatures below 600°K, but the calculated values are systematically low at higher temperatures. The disagreement is by a factor of four at 2000°K, for example. Apparently this discrepancy arises from the method used to estimate the transition probability for combination bands at elevated temperatures; there is no satisfactory way of calculating the effect of vibration interactions on transition probabilities.

The most important qualitative feature of the theoretical and experimental data on the emission from carbon dioxide in the 4.3-micron region at high temperatures is the asymmetric growth of the band toward longer wavelengths. This is evident even at room temperature, where the effect of the quadratic term in the line separation causes the P branch to be spread out and the R branch to be compressed, ultimately to give a band head at 2399 cm^{-1} (4.18 microns). This effect is emphasized at higher temperatures because of the increase in the rotational excitation. In addition, all the hot bands are centered at longer wavelengths because of the effect of vibration on the molecular force constants; these bands also have heads at short wavelength, so the net result is that as the temperature rises, the short wavelength edge of the band remains fixed while the long wavelength limit extends beyond 4.5 microns toward 4.8 and even 5 microns. This long wavelength radiation is extremely important for missile detection and similar applications, as the atmospheric absorption corresponds to the room temperature curves and is small beyond 4.4 to 4.5 microns.

2.3.2   15-Micron v_2 Fundamental Region

Burch (Ref. 2) has published an extensive series of absorption measurements at medium resolution which demonstrate well the character of the carbon dioxide bands in the 15-micron region. A number of these for several absorber concentrations are given in Figs. 2-6 and 2-7.
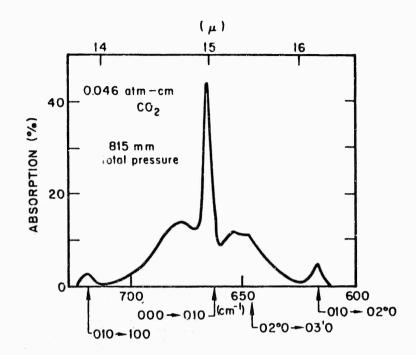
Fig. 2-6 Carbon Dioxide 15-Micron Band Under Medium Resolution, Short Absorbing Path. Data by Burch et al. (Ref. 2)
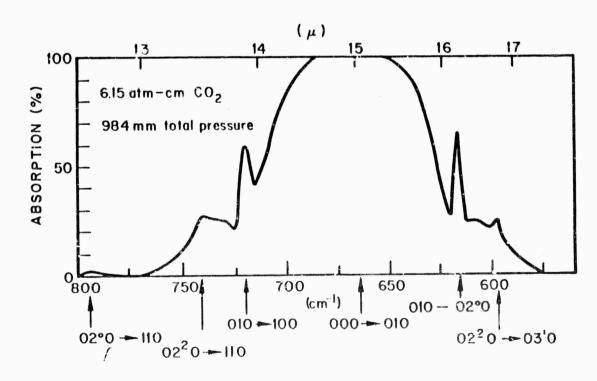

Fig. 2-7 Carbon Dioxide 15-Micron Band, Long Absorbing Path. Data by Burch et al. (Ref. 2)

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Comments:

    (a) The fundamental transition, $(0, 0, 0) \rightarrow (0, 1, 0)$, is between the Σ_g^+ ground state and a Π_u excited state. According to the selection rules, this should show a Q branch in addition to the P and R ; Fig. 2-6 shows this clearly. The width of the band also agrees with theory; the maxima in the P and R branches are about 13 cm^{-1} on either side of the band center (J = 16) as with the 4.3-micron band.

    (b) The longer path lengths show the presence of a number of other bands. These fall into two groups — the $\Delta v_2 = 1$ group, including the fundamental discussed above, and those with $\Delta v_1 = +1$, $\Delta v_2 = -1$, which appear at slightly higher frequencies. All of these bands show a Q branch, as they involve a change in v_2. As an incidental result, the "hot bands" show more clearly for the 15-micron region than for the 4.3-micron region as the sharp peak from the Q branch stands out more than the relatively broad band found when only P and R branches are present.

    (c) It is interesting that Kaplan (Ref. 9) has proposed determining the vertical structure of the atmosphere by satellite observation of the atmospheric emission at ten-wavelength intervals in the 15-micron carbon dioxide band. The great range of absorption coefficient in this band and the presence of a number of hot bands with strong temperature dependence make this band a good choice for these measurements.

2.3.3 2.7-Micron Region

Room temperature. Burch (Ref. 2) has published an extensive series of measurements on this band also. One of these is shown in Fig. 2-8.

Comments:

    • There are two principal bands in this region, $(0, 0, 0) \rightarrow (1, 0, 1)$ and $(0, 0, 0) \rightarrow (0, 2^0, 1)$. Both of these are combination bands; the intensity is therefore comparatively weak compared with the 4.3- and 15-micron
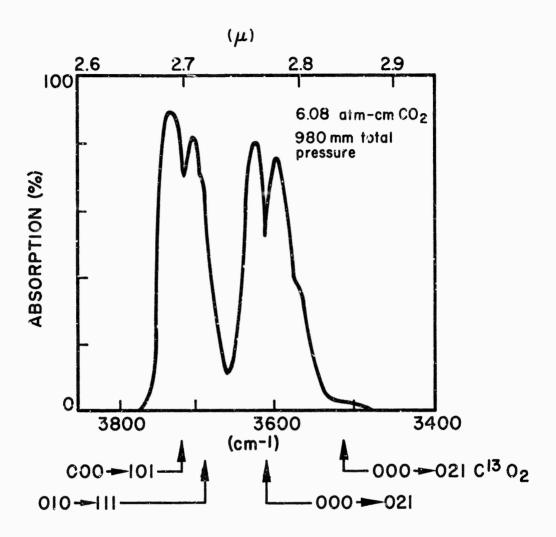
(μ)

Fig. 2-8 Carbon Dioxide 2.7-Micron Bands, Medium Resolution. Data by
Burch et al. (Ref. 2)

fundamental bands as can be seen by comparing curves for comparable absorber
concentration in Figs. 2-2 and 2-7. Both of these bands are $\Sigma_g^+ - \Sigma_u^+$ tran-
sitions, and hence have no Q branch. The separation of the maxima in the
bands is about right; again their peaks are about 13 cm^{-1} from the band centers.

Some evidence appears in the curves for the "hot bands" whose positions are
indicated on the figure, as well as for the isotope band. Plass, in his machine
calculation of the absorption at the 2.7-micron region, included a total of 34
bands, with up to 10 for a given isotope combination; most of these are very
weak.

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- It is interesting to compare the locations of these combination and isotope bands with the approximate locations deduced from the frequencies of the fundamental vibrations:

(1, 0, 1) $v_1 + v_3 = 1388 + 2349 = 3737$ cm^{-1}; observed, 3716 cm^{-1}

(0, 2, 1) $2v_2 + v_3 = 2 \times 667 + 2349 = 3683$ cm^{-1}; observed, 3609 cm^{-1}

The center of gravity of the levels has been shifted down in frequency by 47 cm^{-1} because of the multiple excitation ("looser molecule"), and the separation of the levels has been increased from 54 to 107 cm^{-1} because of the Fermi resonance due to the (v_1, $2v_2$) combination.

- The separation of the normal and isotope bands agrees with theory. The (1, 0, 1) band for $C^{12}O_2^{16}$ is at 3716 cm^{-1}; for $C^{13}O_2^{16}$ it is at 3646 cm^{-1}, a shift of 70 cm^{-1} toward lower frequency. The corresponding values for the (0, 2, 1) band are 3609 and 3504 cm^{-1}, a shift of 105 cm^{-1}. These shifts agree satisfactorily with the values given in Section 2.1 for the three vibrations: 0 for v_1, 19 for v_2, and 68 for v_3.

Elevated temperature. Tourin (Ref. 10) has published emissivity measurements for carbon dioxide in the 2.7-micron region at several temperatures. One of his figures is shown in Fig. 2-9.

Comments:

- Two effects occur as the temperature is increased – the peak band intensity is reduced, and the band spreads out to longer wavelengths. The intensity decrease is primarily due to the decreased density at high temperatures. The band widening is due partly to the higher rotational states involved, but more to the increased intensity of the hot bands with vibrationally excited initial states; these are centered at lower frequencies because of the familiar reduction of force constants as the molecule stretches. As for the 4.3-micron region, the heading up of the R branches of the bands at high values of J prevents the bands from spreading on the short wavelength side.
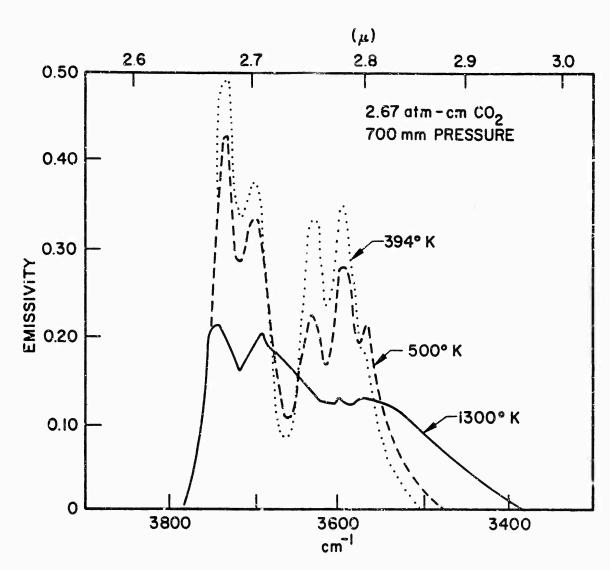
Fig. 2-9 Temperature Dependence of Carbon Dioxide 2.7-Micron Bands.
Data by Tourin (Ref. 10)

2.3.4 Other Bands

A number of other weaker bands of carbon dioxide have been studied by various investigators. Some of these are discussed below.

The 10.4- and 9.4-micron bands. Figure 2-10 shows absorption curves obtained by Burch (Ref. 2) at several temperatures. Figure 2-11 shows lower resolution data reported by Edwards (Ref. 7).
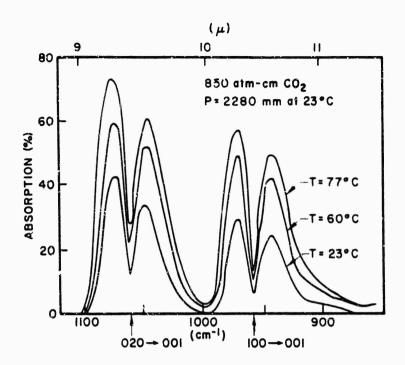
2-28

Fig. 2-10 Carbon Dioxide 9.4- and 10.4-Micron Bands Near Room Temperature.
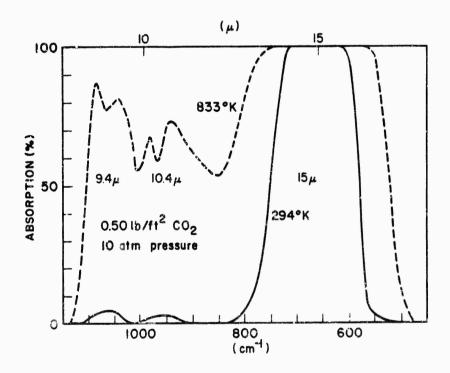Data by Burch et al. (Ref. 2)

Fig. 2-11 Temperature Dependence of Carbon Dioxide 9.4-, 10.4-, and 15-Micron
Bands. Data by Edwards (Ref. 7)

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Comments:

(a) These bands are both hot bands originating from a vibrationally excited state and hence are very weak in absorption at room temperature, but increase in intensity rapidly as the temperature is raised and the (100) and (020) populations increase. The weak absorption is evident from the long absorbing path required for these measurements. In the long-path absorption measurements of Taylor and Yates (Ref. 3), the stronger band absorbs less than 50 percent for a sea-level atmospheric path of 10.1 miles. The bands will be important in emission from high temperature sources, however, as evident from their prominence in Edwards' data at 830°K. They may be important for detection as they fall in a wavelength region of low atmospheric absorption.

(b) Both bands are $\Sigma - \Sigma$ transitions and hence have only P and R branches. They also head up at shorter wavelengths as is evident in Edwards' curves.

Short wavelength bands − 2 microns, 1.6 microns, and 1.4 microns. Figure 2-12 shows data given by Howard, Burch, and Williams (Ref. 4) for these bands. The dependence of the 2.0- and 2.7-micron bands on temperature is shown by Edwards data in Fig. 2-13.

Comments:

(a) All of these bands are very weak because they are combination bands involving rather complicated transitions or, in the case of the 1.4-micron band, are harmonic transitions. As they originate in the ground state, their intensity does not increase rapidly with temperature so, in general, they are unimportant except for long-path atmospheric transmission.

(b) Although the harmonic band $3v_3$ is observed, the first harmonic $2v_2$ is not. This is because the $(0, 0, 0) \rightarrow (0, 0, 3)$ is a $\Sigma_g^+ \rightarrow \Sigma_u^+$ transition and hence is allowed; the $(0, 0, 0) \rightarrow (0, 0, 2)$ transition is $\Sigma_g^+ \rightarrow \Sigma_g^+$ and hence is forbidden. The band $5v_3$ is also allowed but is extremely weak. It does not appear in the absorption in the earth's atmosphere, but is observed in the spectrum of sunlight reflected from the planet Venus, together with the bands $(1, 0, 5)$ and $(0, 2, 5)$.
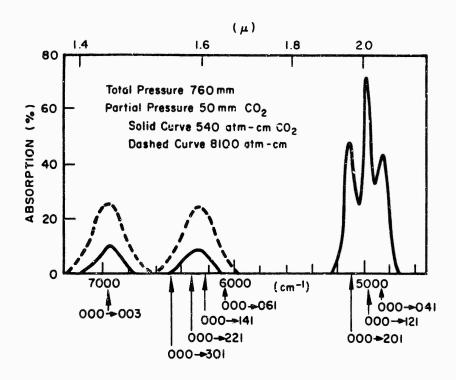
Fig. 2-12 Carbon Dioxide 1.4-, 1.6-, and 2.0-Micron Bands Under Low Resolution.
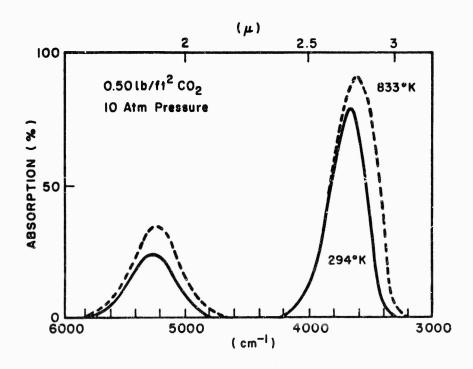Data by Howard et al. (Ref. 4)

Fig. 2-13 Temperature Dependence of Carbon Dioxide 2.0- and 2.7-Micron Bands.
Data by Edwards (Ref. 7)

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(c) There are limited data in the literature for other bands such as those at 7.5 and 1.2 microns, but those are too weak to be of much importance here.

2.3.5 Summary of Carbon Dioxide Bands

In most infrared applications, such as atmospheric transmission and flame emission, the wavelength regions in which carbon dioxide emits or absorbs appreciably are usually designated as the "15-micron band," the "4.3-micron band," and so on. As we have seen, each of these "bands" is actually made up of a large number of individual vibration-rotation bands with different intensities and center frequencies. In absorption at atmospheric temperatures, most of the bands of importance are those which originate from the ground state, (0, 0, 0); of these, the fundamentals are the most intense, with combination bands and overtones usually of much lower importance (except possibly for the "2.7-micron band"). At higher temperatures, "hot bands" in which both the lower and upper states are vibrationally excited become more prominent; those in which the transition is a fundamental or a low order combination can become very important at temperatures encountered in flames and rocket exhausts.

The bands which have been discussed in this report are summarized in Table 2-1. They group themselves in two ways. Each major transition, such as a fundamental, is accompanied by a group of bands of lower intensity in which the same vibration change is involved in the transition but other vibrations are present as well; these satellite bands are of course all hot bands. A second type of grouping arises because of the approximate equality of v_1 and $2v_2$. In the table, the designation (a, b, c), for example, for the vibration change means $\Delta v_1 = a$, $\Delta v_2 = b$, $\Delta v_3 = c$.
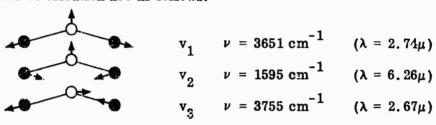
Table 2-1

SUMMARY OF CARBON DIOXIDE BANDS

Band	Vibration Change	Individual V-R Bands	Frequency cm^{-1}	Type	Figure
15 micron	$(0,1,0)$	$000 \to 010$	667	$\perp$	2-6, 2-7, 2-11
		$010 \to 02^00$	618		
		$010 \to 02^20$	668		
		$02^00 \to 03^10$	647		
		$02^20 \to 03^10$	597		
		$010 \to 100$	720		
		$02^20 \to 110$	741	$\perp$	2-6, 2-7, 2-11
	$(+1,-1,0)$	$02^00 \to 110$	791		
10.4 micron	$(-1,0,+1)$	$100 \to 001$	961	$\parallel$	2-10, 2-11
9.6 micron	$(0,-2,+1)$	$020 \to 001$	1063	$\parallel$	2-10, 2-11
5.2 micron	$(0,3,0)$	$000 \to 030$	1932	$\perp$	2-3
		$010 \to 040$	1886		
4.8 micron	$(1,1,0)$	$000 \to 110$	2076	$\perp$	2-3, 2-5
		$010 \to 120$	2094		
	$(2,-1,0)$	$010 \to 200$	2137	$\perp$	2-3
4.3 micron	$(0,0,1)$	$000 \to 001$	2349		
		$010 \to 011$	2337	$\parallel$	2-1, 2-2, 2-5
		$02^20 \to 02^21$	2324		
2.7 micron	$(1,0,1)$	$000 \to 101$	3716	$\parallel$	2-8, 2-9
		$010 \to 111$	3690		
	$(0,2,1)$	$000 \to 021$	3613	$\parallel$	2-8, 2-9
		$010 \to 031$	3617		
2 micron	$(0,4,1)$	$000 \to 041$	4660		
	$(1,2,1)$	$000 \to 121$	4983	$\parallel$	2-12, 2-13
	$(2,0,1)$	$000 \to 201$	5109		
1.6 micron	$(0,6,1)$	$000 \to 061$	6077		
	$(1,4,1)$	$000 \to 141$	6231	$\parallel$	2-12, 2-13
	$(2,2,1)$	$000 \to 221$	6351		
	$(3,0,1)$	$000 \to 301$	6510		
1.4 micron	$(0,0,3)$	$000 \to 003$	6976	$\parallel$	2-12
1.2 micron	$(1,0,3)$	$000 \to 103$	8293	$\parallel$	--
	$(0,2,3)$	$000 \to 023$	8193		

Section 3
WATER VAPOR

3.1 NORMAL VIBRATIONS

The water vapor molecule is a symmetric, non-linear molecule. The three normal modes of vibration are as follows:

v_1 $\nu = 3651 \text{ cm}^{-1}$ ($\lambda = 2.74\mu$)

v_2 $\nu = 1595 \text{ cm}^{-1}$ ($\lambda = 6.26\mu$)

v_3 $\nu = 3755 \text{ cm}^{-1}$ ($\lambda = 2.67\mu$)

All three of these vibration modes are active in the infrared. The fundamental v_1, however, is much weaker than the others. Qualitatively, this is because the molecule is close enough to being linear that the dipole moment in that vibration is very small. (In the linear molecule CO_2, the corresponding mode is completely inactive in the infrared.) The fundamental band v_1 is overlaid by the much stronger band v_3; as we will see, both these bands have very irregular structures and the band v_1 was not positively identified until 1942.

The vibrations v_1 and v_2 can be seen to be symmetric vibrations, with the oscillating dipole moment along the axis of symmetry of the molecule, while v_3 is antisymmetric (with respect to rotation about the axis of symmetry) and the associated dipole moment is perpendicular to that axis.

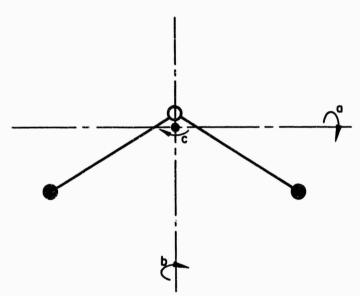The vibrations v_1 and v_3 are very nearly the same frequency, as expected, since they are both essentially O-H stretching vibrations, and the oxygen atom is so much heavier than the hydrogen atoms that it does not partake much in the vibration. These

3-1

vibrations do not perturb each other, as they are of different symmetry character; however, the vibrations $2v_1$ and $2v_3$ have the same symmetry and accordingly are perturbed by Fermi resonance. This circumstance was responsible for much confusion in the early analyses of the water vapor spectrum.

3.2 ROTATION SPECTRUM

3.2.1 Energy Levels

The water vapor molecular rotation is much more complicated than that of carbon dioxide. The latter is linear and has only one rotation mode and one moment of inertia; water vapor has three different moments of inertia about the three axes:

Axis $\underline{a}$ has associated with it the smallest moment of inertia; axis $\underline{b}$, the axis of symmetry, has an intermediate moment, and axis $\underline{c}$, perpendicular to the plane of the molecule, has the largest. Each of these axes has a corresponding rotation constant:

$$A = h^2/8\pi I_a = 27.8 \text{ cm}^{-1}$$
$$B = h^2/8\pi I_b = 14.5 \text{ cm}^{-1}$$
$$C = h^2/8\pi I_c = 9.3 \text{ cm}^{-1}$$

Such a molecule with three different moments of inertia is called an "asymmetric top." Note that the rotation constants for water vapor are much larger than the 0.4 cm^{-1} values for CO_2 because of the small moment of inertia associated with the light hydrogen atoms. As a result, the water vapor spectrum is much more spread out.

As in the case of carbon dioxide or, for that matter, for any molecule, the total angular momentum of the molecule is quantized:

$$M = Jh/2\pi$$

where J is an integer. Each value of J is again associated with $(2J + 1)$ sublevels, but, in contrast to the linear molecule case where all levels with a given J have the same energy, in the asymmetric top all $2J + 1$ sublevels have a different energy. The spread is large for water vapor with its spread of rotation constants. Roughly speaking, the energy values for a given J range from the value $CJ(J + 1)$, corresponding to all the rotation being about the c axis, to $AJ(J + 1)$, which would imply all the rotation about the a axis. For $J = 4$, for example, this would predict a range from 186 to 556 cm^{-1}, compared with the observed 221 to 488 cm^{-1}; for $J = 8$, the approximate limits are 669 to 2001 cm^{-1} compared with the observed 744 to 1789 cm^{-1}. The spacing of the levels between these limits is not uniform, and the rotation levels for different J overlap for values of J larger than three. The net result is a very complicated series of rotation levels, in contrast to the simple progression found in carbon dioxide.

The symmetry of the rotation levels is also more complicated than for carbon dioxide, where alternate levels were + or - with respect to rotation about the molecular axis. Here there are two symmetry operations to consider — rotation by 180 deg about the c axis, and rotation by 180 deg about the a axis. As the molecule has a plane of symmetry (containing the b axis), the wave functions must either be unchanged or change only by a factor (-1) on each of these rotations. This leads to four symmetry classifications — (++), (+-), (-+), and (--).

3.2.2 Pure Rotation Spectrum

Again in contrast to the linear symmetric molecule of carbon dioxide, the water vapor molecule has a permanent dipole moment. (The oxygen atom tends to be negative, and the hydrogen atoms positive.) Water vapor therefore has a pure rotation spectrum. The dipole moment lies along the b axis. The selection rules for this case turn out to be

$$\Delta J = 0, \pm 1$$

$$+ + \longleftrightarrow - - \quad \text{and} \quad + - \longleftrightarrow - +$$

The actual calculation of the spectrum is extremely complicated; in fact, the procedure originally went the other way, with the actual rotation energy levels determined from observation of the rotation spectrum. The situation is complicated further by the high rotation speeds involved for the higher values of J (again because of the light hydrogen atoms, the angular velocity must be large in order to get an angular momentum of $h/2\pi$). This gives a large centrifugal distortion of the levels and can produce level shifts of as much as 280 cm^{-1} for J = 11 .

The net result of all these possible rotation transitions between different sublevels for the various values of J is an extensive infrared "pure rotation" spectrum extending from the neighborhood of 15 microns through the entire far infrared region to the milli-meter wave region. The strongest absorption is in the 50- to 100-micron region; the intensity of the absorption is indicated by the fact that Randall et al. (Ref. 11), who made the most complete study of the band, made their observations by drying the interior of their spectrometer with P_2O_5 and using only the small amount of residual water vapor in the spectrometer as the absorber. They measured 173 lines in the region 18 to 75 microns (74 to 560 cm^{-1}) , for an average line spacing of 2.7 cm^{-1}.

Lower resolution measurements covering the 20- to 40-micron region have been published by Palmer (Ref. 12), and data for the 40- to 2500-micron region have been published by two Russian authors (Ref. 13). The transmission curves are very irregular

and will not be reproduced here. It is interesting to note that the first reasonably trans-parent "window" in the far infrared comes at about 300 microns; the region beyond 1100 microns is clear except for an isolated line at 1634 microns (6.12 cm^{-1} or 1.6 milli-meters), due to the $2_2 \rightarrow 3_{-2}$ transition. This line has been studied both by infrared tech-niques and by microwave spectroscopy (Ref. 14). There is one additional line at longer wavelength (13,500 micron or 1.35 cm, 0.78 cm^{-1}, transition $5_1 \rightarrow 6_{-5}$) which is of his-torical interest because a centimeter-wave radar system developed in 1945 was unfor-tunately centered on this line.

3.3 VIBRATION-ROTATION BANDS

3.3.1 Selection Rules and the Shapes of Bands

The selection rules for an asymmetric top molecule are somewhat different from those for a linear molecule; in particular, the selection rule on J is

$$\Delta J = \pm 1, 0$$

for all bands. All the vibration-rotation bands will, therefore, have P, Q, and R branches. Because of the complicated structure of the rotational energy levels, how-ever, all three branches are very irregular and overlap each other so that, in general, the individual branches cannot be distinguished.

In spite of the complexity of the complete description of these bands, some general statements can be made. The bands for the water vapor molecule can be grouped in two types:

1. Type A bands. In these, the change in dipole moment is in the direction of the smallest moment of inertia of the molecule – that is, along the a axis. As this is perpendicular to the axis of symmetry for the water vapor mole-cule, these are also called perpendicular bands. For these bands, the selec-tion rules regarding the transitions between sublevels are as follows:

$$++ \rightarrow -+ \quad \text{and} \quad +- \rightarrow --$$

The pattern of the symmetry properties of the sublevels for a given J is such that these selection rules tend to emphasize transitions between adjacent sublevels or between relatively distant ones. For the transitions with $\Delta J = 0$, this means that there is a relative excess of these lines with small energy separation from the band center – that is, there is a tendency toward formation of a recognizable Q branch. Not all the Q branch lines are in this central group, and often even this regularity is masked by the difference in rotation constants in the initial and final vibration states; nevertheless, a given band can often be identified as an A band by the indication of the Q branch.

2. <u>Type B bands</u>. In these bands, the change in dipole moment is along the axis with intermediate moment of inertia or the <u>b</u> axis; this is the axis of symmetry for water vapor so they are "parallel" bands. For these bands the rotation sublevel selection rules are:

$$++ \leftrightarrow -- \quad \text{and} \quad +- \leftrightarrow -+$$

These selection rules tend to prohibit transitions between adjacent sublevels for the Q branch with $\Delta J = 0$; this produces a deficiency in transitions with small rotational energy change. The result is a "hole" at the center of the band, usually with two or four secondary maxima adjacent to it. The band looks somewhat like a parallel band for a linear molecule; in this case, however, there is actually a Q branch which is spread out so that it cannot be identified as such.

3.3.2 The 6.3-Micron v_2 Fundamental Band

Spectral measurements of this band have been reported by Burch et al. (Ref. 2) using medium resolution, and by Howard, Burch, and Williams (Ref. 4) using low resolution. Sample curves from their reports are shown in Figs. 3-1 and 3-2.
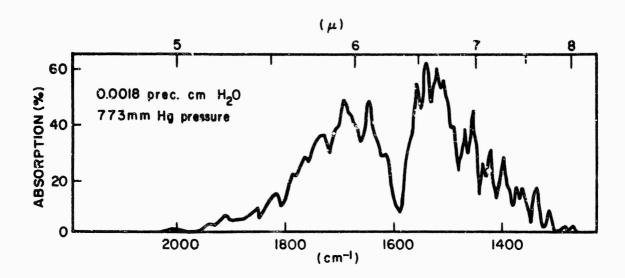
Fig. 3-1 Water Vapor 6.3-Micron Band Under Medium Resolution.   Data by Burch
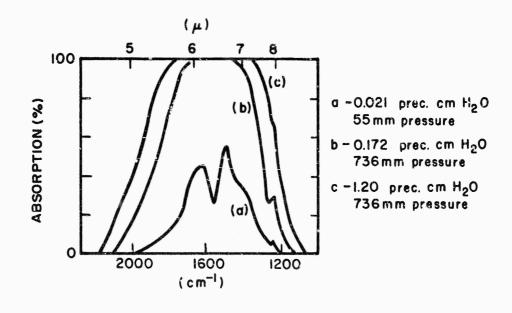et al. (Ref. 2)

Fig. 3-2 Water Vapor 6.3-Micron Band Under Low Resolution.   Data
by Howard et al. (Ref. 4)

3-7

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Comments:

(a) It is evident from the medium resolution curves that this band is indeed a very complicated one. Under higher resolution it is much more so; Nielson (Ref. 15) measured 112 lines just in the region from 1490 cm^{-1} to 1760 cm^{-1}, and many of these were superpositions of as many as four individual lines which he could not resolve.

(b) This is a Type A band, with the oscillating dipole perpendicular to the symmetry axis. According to the previous section, this band should have an intensity minimum at the center, which it does.

(c) The width of this band is much larger than the width of carbon dioxide bands — the maxima are 50 to 100 cm^{-1} from the band centers rather than 13 as in CO_2, and the total band width is much greater. This is a result of the lower moments of inertia for the water vapor molecule, with correspondingly larger rotation constants; a contributing factor is the more complicated rotational level structure with a wide variety of possible transitions as compared with transitions only between adjacent rotational levels in carbon dioxide. Because of the spread-out structure, the apparent band width becomes large for large amounts of absorber. The atmospheric transmission curves of Taylor and Yates show complete absorption over the region 5.5 to 7.2 microns (1390 to 1820 cm^{-1}) for a water vapor content of 5.7 prec. mm; from 5.1 to 7.7 microns (1300 to 1960 cm^{-1}) for 5.2 prec. cm; and from 4.95 to 8.0 microns (1250 to 2020 cm^{-1}) for 20 prec. cm of water. These band widths contrast with a maximum width of 190 cm^{-1} for the carbon dioxide 4.3-micron band over their longest path.

(d) To the knowledge of the writer there are no published data on the 6.3-micron water vapor band at elevated temperatures. Inspection of the rotation level assignments given by Nielson (Ref. 15), however, shows that lines with high J are scattered through the band. The lines farther from the center tend to come from levels with higher J, however, so one would expect that an increase in temperature will cause the band to spread to some extent, in addition to changing the detailed shape throughout the band.

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3.3.3 The 2.7- and 3.2-Micron Bands

Medium resolution measurements by Burch, et al., and low resolution measurements by Howard, et al., are shown in Figs. 3-3 and 3-4.
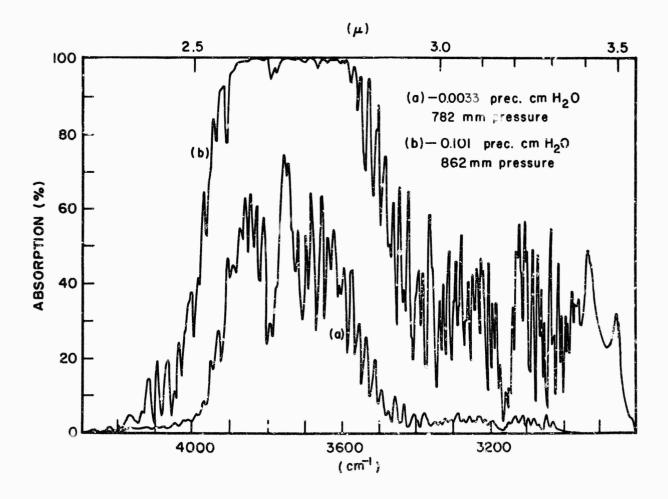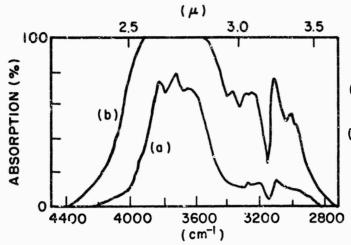
Fig. 3-3 Water Vapor 2.7- and 3.2-Micron Bands, Medium Resolution. Data by Burch et al. (Ref. 12)

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Fig. 3-4 Water Vapor 2.7- and 3.2-Micron Bands Under Low Resolution. Data by Howard et al. (Ref. 4)

Comments:

(a) The comments regarding band complexity apply here as well.

(b) The 3.2-micron band is the first overtone band of v_2 . The band $2v_2$ was forbidden in carbon dioxide by the g , u symmetry rule; water vapor has no center of symmetry so this band is allowed although it is relatively weak compared with the fundamentals. It is again a Type B band and shows a pronounced intensity minimum at the center.

(c) The main structure in the 2.7-micron band is due to the fundamental v_3 , centered at 3755 cm^{-1}. This is an A band, and the "Q branch" at the band center is evident. The detailed structure in this region is very complicated; Nielson (Ref. 16) identified over 200 lines in a 400 cm^{-1} interval, and many of these were multiple. In this process, there were a considerable number of lines which did not fit into the v_3 rotation structure; he was able to identify these as transitions in the v_1 fundamental band. This was the first definite identification of the v_1 band, which is thoroughly mixed up with the much stronger v_3 band. v_1 is a B band, but the intensity minimum at its center is obscured by lines from the v_3 band.

(d) Tourin (Ref. 16) has recently published absorption curves for the 2.7-micron water vapor band at elevated temperatures. These show that the shape of this band does not change greatly over the range from 0 to 1000° C. The observed absorption increased somewhat in the outer regions of the band compared to the center, but the overall appearance and structure remained about the same. This is in agreement with comment (d) made in Section 3.3.2 on the basis of the distribution of the lines from different rotational levels. A second reason, pointed out by Tourin, for the relatively small change of the water vapor band over this temperature range compared to the change for the 2.7-micron carbon dioxide band lies in the character of the hot bands. The lowest vibrational state of water vapor is at 1595 cm^{-1} (6.3μ) for carbon dioxide. At 1000° C, therefore, most of the water vapor is still in the ground state, and the broadening effect of hot bands, so prominent in the carbon dioxide spectrum shown in Fig. 2-9, is virtually absent.

3.3.4 Combination Bands at Shorter Wavelengths

There are a considerable number of bands at shorter wavelengths which are important in atmospheric absorption problems. Some of these were studied by Howard, Burch, and Williams; their published curves are at low resolution, however, and since they do not show any interesting detail they will not be repeated here. Many of these bands are evident in Fig. 3-5 which shows atmospheric transmission curves obtained by Taylor and Yates. The three curves are for the following paths: (a) 1000-foot path containing 1.1 prec. mm water vapor; (b) 3.4-mile path containing 13.7 prec. mm water vapor; and (c) 10.1-mile path containing 52.0 prec. mm water vapor. All of these bands are Type A bands, and in most cases would show some sort of central maximum at high resolution. All of them originate from the ground state, (0, 0, 0). In addition to the bands shown in the figure, there are a number of higher order transitions extending well into the visible region. These are all very weak, but they played an important part in the original analyses of the water vapor spectrum as they can be studied with a very long absorbing path (using the sun as a source) and high-resolution photographic techniques can be used to study the bands in detail.
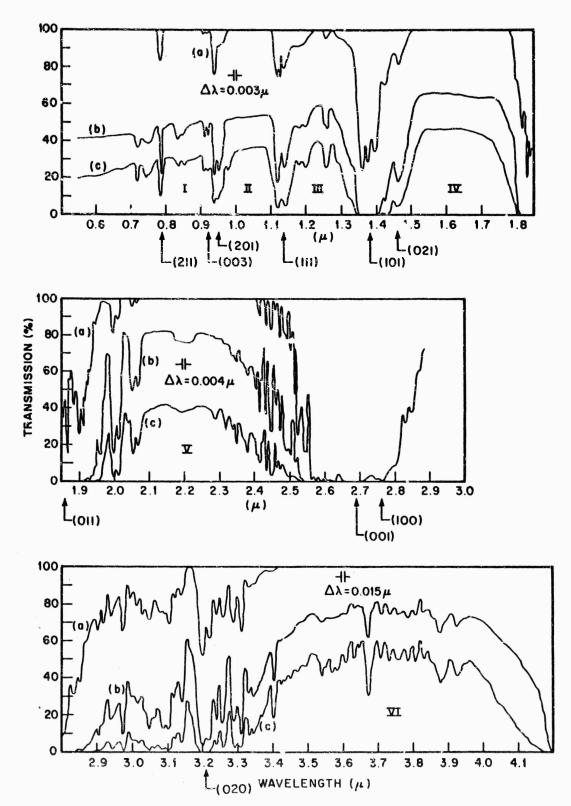
Fig. 3-5 Long-Path Atmospheric Transmission Curves, Showing Locations of Water Vapor Absorption Bands. Data by Taylor and Yates (Ref. 3)

3-12

Section 4
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